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Ammonia sensors based on suspended silicon nanowires

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Abstract

Resistors based on parallel suspended polycrystalline silicon nanowires are fabricated using the classical top down CMOS silicon technologies. Results show potential use as sensitive units of silicon nanowires for charged chemical species (ammonia) detection. Resistors are promising as low-cost manufacturing gas sensors, for very high sensitive ammonia detection over a large concentration range.

Keywords: suspended silicon nanowires; CMOS compatible; ammonia sensor, sensitivity;

1. Introduction

Owing to their physical and electrical properties, semiconducting nanowires are the subject of intense research activities. In particular, silicon nanowires (SiNWs) are fully compatible with the high reliable well known CMOS (Complementary Metal Oxide Semiconductor) silicon technology. In addition, thanks to their high surface to volume ratio, SiNWs are good candidates for fabrication of high sensitive chemical sensors [1,2].

SiNWs can be prepared by one of two approaches, "top-down" or "bottom up". In a bottom up strategy the individual base elements (atoms, molecules…) of the system are linked together to form larger subsystems. The main drawbacks of these synthesis methods for a 3D integration are the difficulty in control of size and positioning of the nanowires. In this case, nanowires need to be selectively collected and manipulated to be assembled in a planar layout. The "top down" approach starts from bulk materials and scales down the patterned areas. In this way, several advanced lithographic tools with nanometer size

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resolution rest on the high cost generated, and more generally the low throughput capability is unsuitable with mass production.
In this work polycrystalline silicon (polysilicon) nanowires based resistors used as gas (ammonia) sensors are fabricated. Nanowires are synthesized following the top down approach, using a classical fabrication method commonly used in microelectronic industry: the sidewall spacer formation technique. Assets of this technological process rest on low cost lithographic tools, classical silicon planar technology compatibility, and the possibility to get numerous parallel nanowires with precise location on the substrate.

2. Devices fabrication

Polysilicon nanowires fabrication is illustrated in the figure 1. A (100) oriented silicon substrate is first capped with 1.5µm thick SiO_2 layer deposited by APCVD (Atmospheric Pressure Chemical Deposition) technique at 420°C, patterned and dry-etched to realize a 100nm thick step. Then, a polysilicon layer is deposited by CVD technique at low pressure (LPCVD) at 550°C and crystallized at 600°C. Dry etching control of the polysilicon layer allows the nanowires formation made of residual polysilicon (spacer) in the step side.

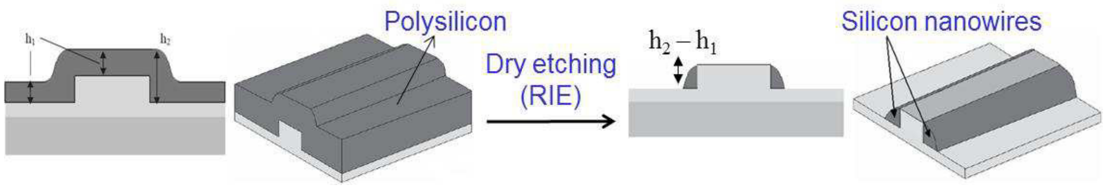

Fig. 1: Schematic view of the fabrication of the (sidewall spacer) polycrystalline silicon nanowires

Two types of resistors (fig. 2) based on grounded or suspended SiNWs are studied as gas (ammonia) sensors. Resistors process fabrication is compatible with a mass production planar layout. In this case, a polysilicon layer with two differently doped stack regions is deposited on the SiO_2 step: the lower part is undoped and the upper part is highly *in-situ* doped with phosphorus. A patterning by plasma etching of this polysilicon layer is achieved to both create spacers (undoped polysilicon nanowires) and electrodes (highly doped polysilicon) of the resistors. A wet etching of the SiO_2 layer allows the suspended SiNWs formation anchored between two highly doped Si electrodes (fig. 2. b). Figure 3 shows the SEM image of 100nm radius curvature suspended polysilicon NWs based resistor. Electrical characteristics of these devices were previously reported [3].
Because SiNWs act as sensitive units, suspended SiNWs based device offers larger sensing area.

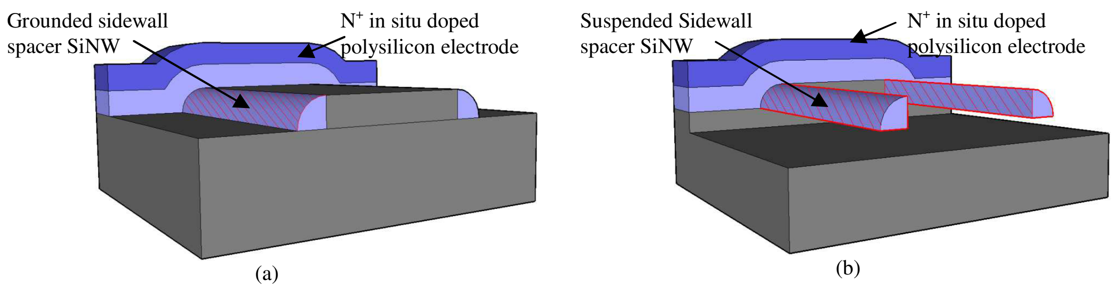

Fig. 2: Schematic view of grounded (a) and suspended (b) sidewall spacer polycrystalline SiNWs based resistors

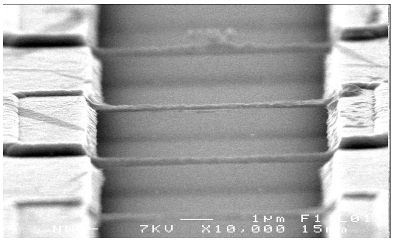

Fig. 3: SEM image of suspended polycrystalline SiNWs based resistor.

3. Results

3.1 Methodology

Gas (ammonia) detection is carried out measuring the current whereas the voltage of the DC source is fixed at 1V. The deduced R-values are then reported as function of time for devices under exposure to ammonia. Prior to measurements, a highly diluted hydrofluoric acid (2 %) aqueous solution based wet etching is used to remove the native oxide on the SiNWs surface in order to promote chemical species adsorption. Then, SiNWs based devices are put into a vacuum chamber. Electrical measurements are carried out at room temperature and the pressure is monitored at 500 mbar regardless of the gas (ammonia) flow injection. Before beginning the sensing measurement, a degassing process is carried out at 200°C for one hour, which permits to eliminate the impurities adsorbed at the nanowires surface that will influence the conductivity. The sample is then cooled down to room temperature.

At first, a flow of nitrogen gas is injected continuously into the chamber during few minutes to guarantee current baseline levelled off. Then, a flow of ammonia is injected with the chosen dilution of NH_3/N_2 during a few minutes. The gas injection is cut off and the gas mixture of NH_3/N_2 is evacuated by pumping afterwards. During the whole period of measurement, gas mixture is exchanged all the time whereas the concentration of the gases is kept constant.

The potential use of the SiNWs based resistors as ammonia sensors was checked by measuring the detection response, S_g, defined as:

$$S_g(\%) = \left| \frac{R_g - R}{R_g} \right|$$

where R and R_g are the resistance values for devices under nitrogen and reactive ambience, respectively.

3.2 Ammonia detection

Previous results [4,5] showed that for dynamic measurements, that consist in exposing SiNWs based resistors under various ratio of ammonia (from 2 ppm to 700 ppm) at room temperature, resistance decreases (current increases) under exposure. The mechanism of such sensors is explained by two main theories, charge exchanging effect and chemical gating effect. This effect is explained by charges exchange between the adsorbed molecules and the SiNWs. It means that the NH_3 molecules adsorbed on the surface of the SiNWs could transfer charges following the equation: $NH_3 \rightarrow NH_3^+ + e^-$ due to the reducing effect (electron donor) of ammonia. This phenomenon could directly inject electron carriers into the SiNWs, thus decreasing the resistance [6,7]. Moreover, as SiNWs conductance can be modulated by an applied voltage, positively charged gas molecules (electron donors) bound on SiNWs surface can modulate their conductance by changing the volume of the conductive layer. In this case, the adsorbed gas molecules, NH_3^+ may act as chemical gates which shift the Fermi level of the undoped SiNWs in the upper part of the band gap and reduces the resistance of the VLS SiNWs based device.

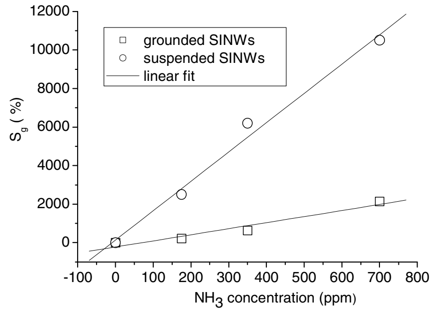

Fig. 4: Relative response of de sensors vs the ammonia concentration for suspended, grounded SiNWs resistors

For each NH_3/N_2 gas mixture, maximum values of S_g are calculated and reported in figure 4. Results show that S_g increases as the NH_3 concentration increases following a linear behavior over a wide range of gas (ammonia) concentration. In this case, gas sensor relative sensitivities, defined as $S=\Delta S_g/\Delta NH_3$ are estimated and reported in to table 1. Results shows that S is higher for suspended based SiNWs based devices because of a higher surface exchange.

Table 1: Values of the relative sensitivity to ammonia for grounded and suspended SiNWs based resistors

	Grounded SiNWs based sensors	Suspended SiNWs based sensors
Relative sensitivity (%/ppm)	4	15.1

4. Conclusion

In conclusion, we present the process fabrication of two different configurations of resistors based on SiNWs using classical silicon planar technology. We demonstrate that their performances under exposure show a linear response over a wide range of ammonia concentration. The study highlights that the relative sensitivity is higher for suspended SiNWs based sensors due to a higher exchange surface.These results show potential use of these SiNWs based devices for charged chemical species (ammonia) detection in a fully compatible silicon CMOS technology.

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